Synchrotron Radiation Instrumentation Collaborative Access Team

SRI CAT NEWSLETTER

Vol. 3, No. 3 April 1997

From the desk of the Executive Director:

The SRI CAT "Annual" Meeting that was held at Argonne January 8 and 9, 1997, was a particularly gratifying one for me personally. After having organized and run several previous Annual Meetings discussing beamline designs and installation plans, it was a pleasure for me to introduce speakers who were presenting experimental results collected on the various beamlines. I appreciate the effort of the local staff to take the time to make the presentations and attend the meeting (there was User beam scheduled during the meeting) and thank those off-site members who had to travel from their home institution to attend.

Although the main focus of the Annual Meeting was scientific results, part of it was devoted to updating the membership on our plans for Sector 4 Development. Current plans call for this insertion-device-based beamline to be used primarily for generation and use of polarized x-rays from 0.5 keV to 50 keV. A helical undulator is planned to produce variable polarized x-rays from about 0.5 to 5 keV, while single- crystal optical components will be used to manipulate the polarization from undulator A in the higher energy regime. In addition to suitability for polarized x-ray experiments, the proposed beamline has been designed to incorporate several other capabilities that are not available on any of the existing SRI CAT beamlines in Sectors 1, 2, & 3. We are planning to move the existing hard x-ray polarization program from Sector 1 and the soft x-ray spectroscopy program from Sector 2 to Sector 4, thus alleviating some of the scheduling pressures on those two sectors.

Before leaving the Annual Meeting and going on to other topics, let me extend my apologies to you if you are a Scientific Member of SRI CAT and did not get a notification of the Annual Meeting. During the secretary shuffle (see below), I grabbed an outdated list of scientific members and used that for the meeting notification mailing. It was only after the meeting that I realized my error.

On January 20, 1997, SRI CAT updated the Program Evaluation Board (PEB) on the progress of work in Sectors 1, 2, & 3 and of our plans for Sector 4. The PEB was very pleased with our progress and pointed out that the SRI "...CAT is definitely on track and has already made excellent progress in fulfilling its mission." Congratulations go to both beamline support staff and lead scientists on a job well done. The PEB has requested that SRI CAT prepare a scientific proposal for Sector 4 for presentation at the next PEB meeting on May 30, 1997. We have already begun this process and should have a solid proposal ready by the beginning of May.

As you may already know, Laura Miller accepted a promotion to become the Executive Secretary for the IPNS Division Director in November 1996. Linda Shoudis has accepted our offer for the position of CAT Secretary and joined SRI CAT in March. Linda comes to us from the Experimental Facilities Division Office. Please take the time to introduce yourself to her and welcome her to the SRI CAT. Between Laura's departure and Linda's arrival, Sue Sarvey covered our secretarial needs and on behalf of all the SRI members I would like to thank her for doing an outstanding job.

And one last acknowledgment, I would like to express my appreciation to Ian McNulty for serving as the Co-Editor of the SRI CAT Newsletter from its inception. He is stepping down and Derrick C. Mancini will be taking his place starting with this issue. Thanks Ian for chasing down all those articles and harassing the staff to be sure the articles were in on time.

D. M. Mills, Executive Director, SRI CAT

Table of Contents

Analyzing Optics for High Resolution Inelastic X-Ray Scattering (HRIXS)

Introduction

HRIXS is a very new technique for studying low energy excitations in liquids and solids, a field of research traditionally studied using inelastic neutron scattering (INS). HRIXS is designed to complement INS. The current state-of-the-art optics for HRIXS is the result of ten years of development starting with the first instrument designed by Dorner, Burkel et al. Peisl in 1986 [1]. Even though Burkel et al. [2] were able to collect data on phonons in beryllium and diamond, further improvements were limited by their large divergent radiation source (wiggler). The new generation of instruments at the Advanced Photon Source (APS) and the European Synchrotron Radiation Facility (ESRF) are using well-collimated X-rays emitted by an undulator.

Developing analyzing optics for HRIXS is still a challenge and is still the energy-resolution-limiting optical component. The basic idea of a high-energy-resolution analyzer comes from INS. Alefeld et al. [3,4] built the first high-energy-resolution analyzer for INS using backscattering geometry. Later (in 1982) Graeff and Materlik [5] showed that using Si(nnn) back reflection for X-rays combined with temperature-controlled lattice spacing, one can achieve energy resolution of the order of the Darwin width. Synchrotron radiation sources provide the required flux and the continous spectrum to take advantage of those back reflections.

The flux of momentum-resolved inelastically scattered photons is low because of the small cross section. Therefore, one likes an analyzer that covers a particular solid angle, i.e., a focusing optic. The need for focusing limits the achievable energy resolution.

Development of an Analyzer for HRIXS

In designing a focusing analyzer for X-rays, one could start from a spherically bent single crystal. Preferably one uses silicon or germanium wafers, since these are available in perfect crystals. Perfect crystals are required, otherwise one does not reach back reflections of intrinsic Darwin width. Unfortunately, while bending the crystals, the width of back reflections is broadened by strain in the crystal. In addition to the idea of a double-radius bent crystal, which deals with compensating strain fields [6], the current work focuses on relieving strain in perfect crystals. Different methods exist to solve this problem.

The first kind of strain-relieved analyzer (developed by Burkel et al..[2]) was a diced silicon wafer with a thin backwall left pressed into a concave glass substrate. Significant strain was left leading to strain-broadened energy resolution of a few times the Darwin width (typically the Si(888) reflection). X-rays reflected in the grooves by the back wall carry a major part of the strain broadening. The same group started to combine a silicon wafer with a glass wafer to avoid strain contributions from the silicon backwall.

The diced face of the silicon wafer was bonded to a flat glass wafer using anodic bonding (done at the Fraunhofer Institut für Festkörpertechnologie). Then, the remaining back wall of the silicon wafer was removed by etching. In the end, there was a glass wafer with stand-alone silicon blocks left, which when pressed and glued into the substrate led to an analyzer giving an energy resolution twice as big as the Darwin width. Development of this design was continued at the ESRF. Instead of using anodic bonding and an intermediate glass wafer, Sette et al.[7] pressed and glued the diced face of the silicon wafer directly to the concave glass substrate and then removed the back wall by etching. This method requires strong etchant, which forces one to use etch-resistant epoxy. Etch-resistant epoxy itself creates strain in the silicon. Therefore, it is necessary to reduce the amount of epoxy to a minimum. This challenge was solved by constructing a device that puts small drops of epoxy on each block of the diced face (about 7500 blocks). The technique provides an analyzer with an energy resolution twice the Darwin width using the Si(999) reflection [7].

At Sector 3 at the APS, we have started three new kinds of analyzer designs: first, the already mentioned method using strain-compensating fields, second, silicon-on-silicon bonding [8], and third, silicon on glass/glass.

The idea of using strain-compensating fields follows from the fact that one can avoid strain along the lattice spacing of the reflection by taking advantage of the elastic anisotropy in silicon. Bending with two different radii along properly chosen directions leads to the desired superposition of strain fields. This technique requires high precision crystal orientation. First results have shown that the accuracy is still not high enough. Such an analyzer has the advantage that there is no loss in reflectivity due to dicing.

The silicon-on-silicon bonding does not need any glue. The surfaces of the Si substrate and Si wafer must be of perfect finish. The direct bonding between silicon atoms starts at high temperatures. One analyzer exists in which the thin backwall has been directly bonded to the concave Si-substrate. This analyzer has a perfect figure. Its energy resolution achieved to date is about 1.5 times the Darwin width using the Si(777) reflection.

The silicon on glass/glass analyzer, so far, is the easiest way to make a strain-relieved analyzer (Figure 1). One glues a silicon wafer to a flat glass wafer using epoxy 301, which cures at

room temperature. After dicing through the silicon into the glass, a back wall in the glass is left. The diced 'sandwich' is to be pressed and glued to the substrate. The glass is much softer than the silicon; less stress is the result. The difference in Young's modulus between glass and silicon ($E_{glass} < E_{silicon}$) leads to less strain in the silicon. Furthermore, the epoxy layer between the silicon blocks and the glass absorbs strain gradients. In recent measurements using the Si(777) reflection, the overall energy resolution obtained with this analyzer was 9 meV (see Figure 2).

Outlook

The need for further development of analyzers has not yet come to an end. The technique presented at the ESRF provides analyzers with energy resolution of about 2 meV. But, this happens at a high cost of flux. Time-consuming data collection (many hours per spectrum) is the result. The analyzer reflectivity suffers from intense etching.

The new 'sandwich' analyzer developed at the APS leads to good energy resolution and high reflectivity. So far, this has been proven at the Si(777) reflection. However, a final characterization can be made only by using higher order (hhh) reflections.

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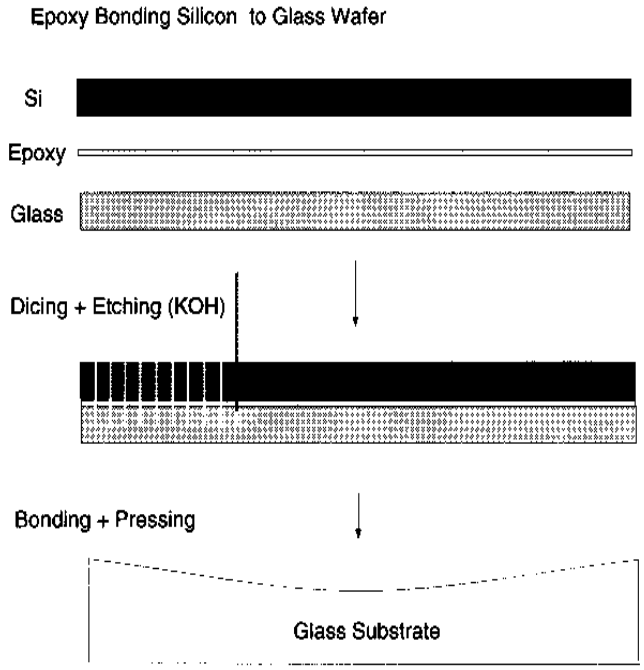

Fig. 1 Processing of a silicon on glass/glass 'sandwich' analyzer.

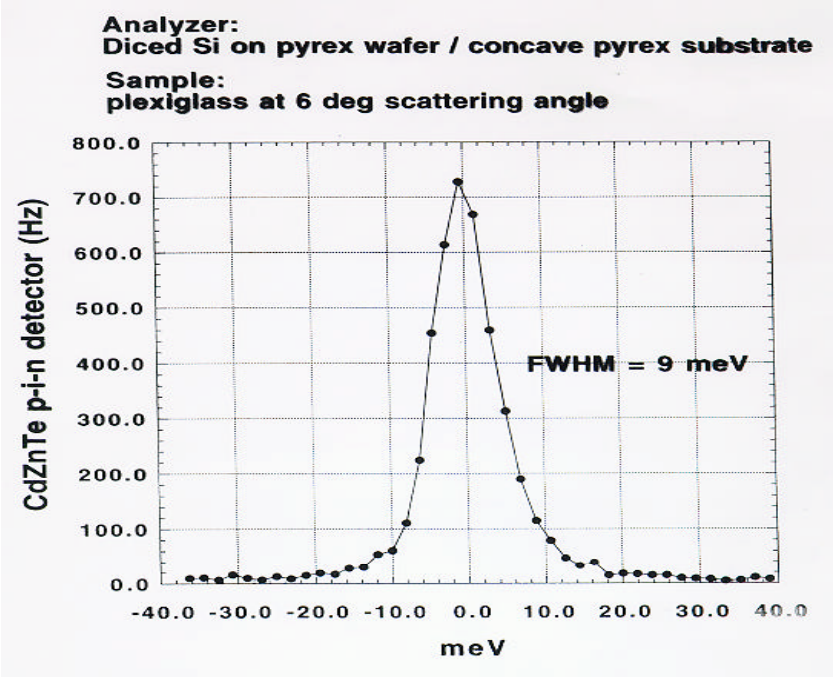

Fig. 2 Overall resolution function of monochromator and analyzer using elastic scattering from plastic.

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Micromachining Using Deep X-Ray Lithography on Beamline 2-BM

Introduction

With a critical energy of 19.5 keV and a highly collimated beam (< 0.1 mrad), the APS is well suited for producing high-aspect-ratio microstructures in thick resist films (> 1 mm) using deep x-ray lithography (DXRL).[1] The high critical energy of the bending magnet radiation makes possible the fabrication of very thick structures or parallel exposure of many samples. The high flux available even at energies above 10 keV will greatly reduce the exposure time for thick resists composed to softer sources. Another important factor is the high precision with which the structure can be replicated by the lithography process, due to the small source size, large distance from the source, and natural collimation of the x-ray beam. The 2-BM beamline was designed to exploit these benefits and to advance the capabilities of DXRL. Initial applications include x-ray optical elements of interest to the APS user community and advanced accelerator structures.

The process of fabricating microstructures using DXRL is showed schematically in Figure 1. The x-ray mask consists of patterns defined by an absorbing material (usually Au) supported on a thin plate (Be, Si, etc.). The pattern is then transferred to the resist layer using x-ray proximity exposure. A widely used photoresist is polymethylmethacrylate (PMMA). To obtain a uniform exposure, the mask and resist are scanned together through the x-ray beam in the vertical plane. After exposure, the resist is developed in organic solvent, the final structures are electroformed onto the substrate, and the remaining resist is stripped away. While soft x-ray lithography is being exploited mainly for the high precision it offers in the pattern transfer process, an additional benefit of DXRL is the higher aspect ratio in the final structure relative to the original mask.

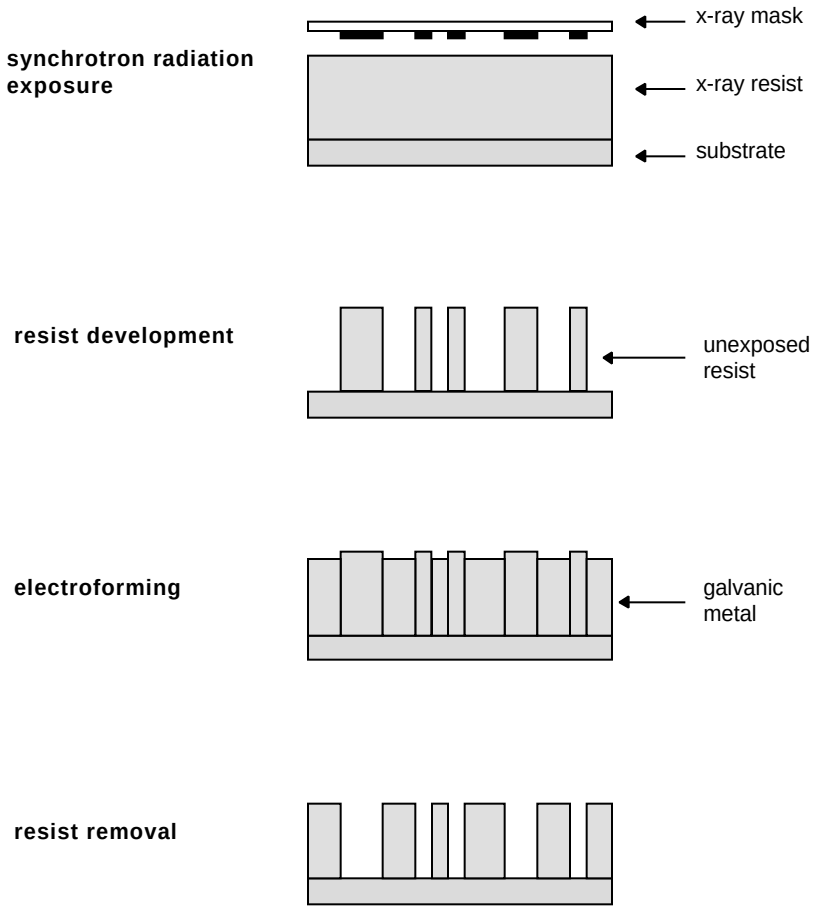

Fig. 1. Schematic of the DXRL process: exposure, resist development, electroforming, and resist stripping. Note the final structure has a higher aspect ratio than the mask.

Requirements

Many factors can affect the quality of the final microstructures, such as mask contrast and stability, resist photochemistry, resist/developer chemistry, substrate and overlayer adhesion, and electroforming conditions; changes in one parameter typically affect several others. Among them, the exposure condition is determined mainly by the beamline and scanner configuration, material and geometry of the mask and resist, and the desired microstructures. For instance, the thickness of gold on the mask should be > 30 mm, in order to provide adequate contrast (> 50:1) between the exposed and unexposed regions of the PMMA. Within the exposed region, the absorbed dose ratio should be uniform along the depth (preferably < 2:1) of the resist. This limits how soft the x-ray spectrum can be. For PMMA, the absorption length is 1 mm for 7 keV x-rays and 10 mm at 15 keV. On the other hand, x-rays that are too hard will require thicker gold

absorber on the mask, increase scattering in the mask and resist/substrate, and prolong the exposure time.

Thus the x-ray spectrum needs to be adjusted, depending on the mask and resist thickness. The minimum absorbed dose required on the exposed PMMA is ~5 kJ/cm^3 for proper development afterward. To provide this dose within a reasonable exposure time of 1-3 hours, a wide energy band spectrum is used for exposure. Another requirement is the scanner should be able to expose a 4" wafer or a 10x10 cm^2 area in a single field. The scanner speed should be 100 mm/s or higher, in order to reduce the local thermal distortion on the mask and resist. During scanning, the angular deviation of the mask/resist relative to the x-ray beam should be < 0.1 mrad, in order to maintain a lithographic accuracy of 0.1 mm for a 1-mm-thick resist.

Beamline Design

The 2-BM beamline (Figure 2) provides the flexible spectral tuning and broad-band radiation necessary for DXRL by using x-ray filters to vary the low-energy cutoff and mirrors for the high-energy cutoff. The beamline accepts 2 horizontal mrad of the radiation. The filter assembly (F2-20) consists of eight graphite and aluminum foils mounted on two actuators and allows the low-energy cutoff to be adjusted between 2 to 15 keV. The first mirror (Y3-30) is a flat, vertically deflecting mirror that is 1.2 m long with a fixed incident angle of 0.15°. There are two strips of coating on this mirror: Pt-cutoff at 33 keV, and Cr-cutoff at 20 keV. The Pt coating may be used to expose photoresists up to several centimeters in thickness. For thinner resists, the Cr coating eliminates the high energy x-rays, which reduces thermal load and scattering and enhances the mask contrast. By locating the first mirror in the FOE, synchrotron radiation may be separated from the bremsstrahlung radiation and be transported to the 2-BM-B experimental station. Exposure will normally be carried out in the B station, but provision to expose in the FOE is also available when higher beam intensity is required.

A second mirror (Y3-20) and the scanner are located in the 2-BM-B station. In some cases, such as using a low contrast mask (gold < 30 mm) for exposing thin resists or fabricating additional masks, a high-energy cutoff below 20 keV is desired. This is accomplished by using the second mirror, without disturbing optics in the FOE or the transport itself. The mirror is Pt coated, and the incidence angle can be adjusted. With the scanner located right

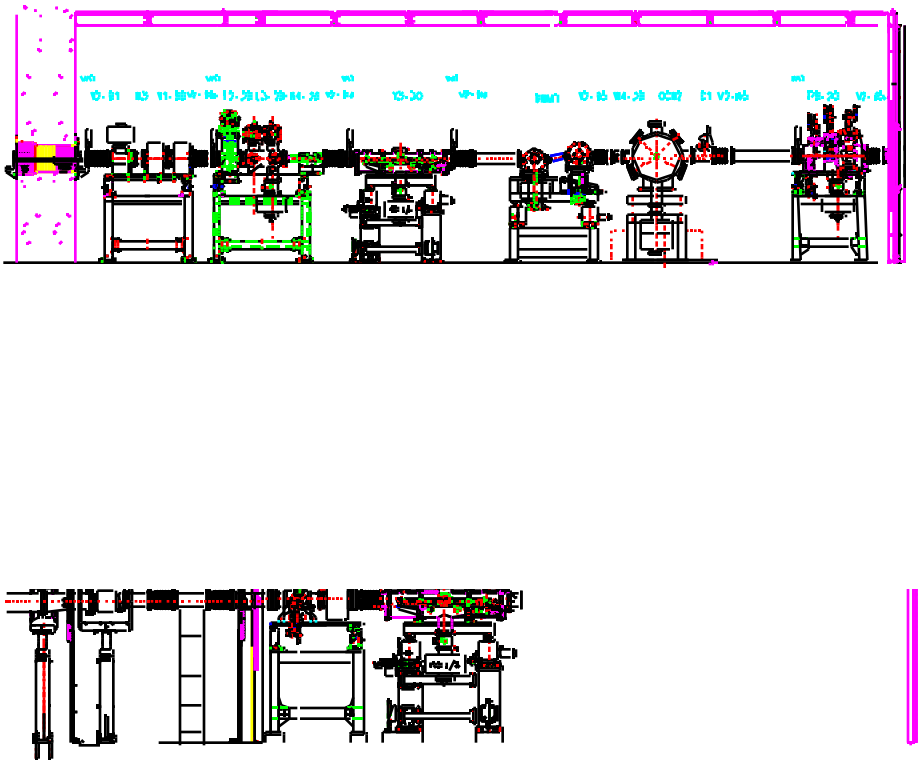

Fig. 2. Layout of the 2-BM beamline.

after the second mirror, it can easily follow any angular or positional change in the beam due to the second mirror. At the scanner, the beam size is 100(H) x 5(V) mm^2. Uniform exposure is achieved by a high-speed (100 mm/sec) vertical scanner. In addition to the vertical motion, the scanner consists of a horizontal translation, for field stitching and general alignment, and two rotation stages, for generating inclined, conical, pyramidal, or other profiles. The scanner allows precise angular (~ 0.1 mrad) and positional (< 1 mm) control of the sample, allowing full use of the highly collimated beam for lateral accuracy and control of side wall slopes during exposure of thick resists. For 1-mm-thick PMMA, a 100 x 25 mm^2 area can be fully exposed in < one hour, while even 10-mm-thick PMMA will require only 2-4 hours.

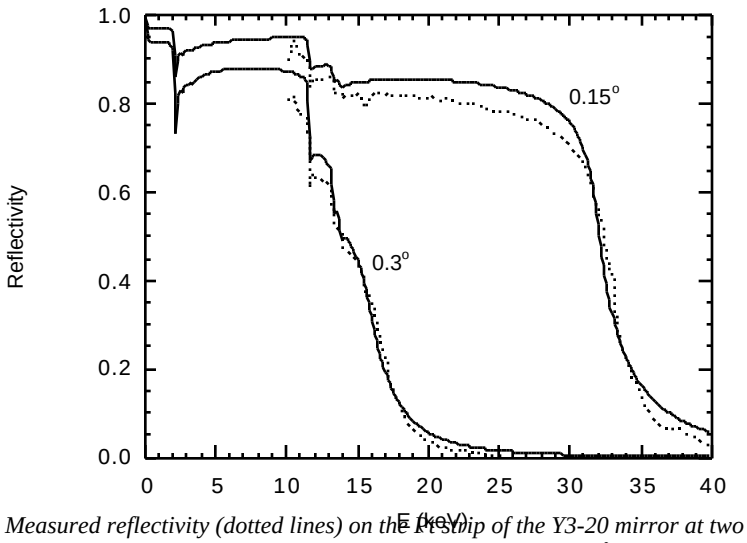

Fig. 3. Measured reflectivity (dotted lines) on the Pt strip of the Y3-20 mirror at two angles of incidence. Calculation (solid lines) with a roughness of 2.4 Å rms included.

Recent Results

The beam transport and the PSS verification for both stations have been completed. The B station has just gone through a radiation survey and should be available for use upon mitigation. The P6 integral shutter, L3 and L4 slits, F2 filter, collimator, and differential pump have all been installed. The Y3-20 mirror was temporarily installed in the FOE, in place of the Y3-30 mirror, which will be ready by summer 1997. Exposure had been performed in the FOE using a prototype scanner, which provides initial characterization of various processes in DXRL. An EPICS-based exposure control has been developed to integrate the scanner operation with other beamline controls and to automate the exposure.

Diagnostic measurements have been carried out to characterize the performance of the mirror and the filters. Figure 3 shows the reflectivity measured for the Y3-20 mirror. The measured and calculated reflectivity agree within 5% at both angles. At 0.15ß, the reflectivity is better than 80% at most energies and is about 70% at 30 keV. Several filter transmission spectra have been measured to obtain the effective filter thicknesses (optical densities). One critical result is that the 1 mm graphite filter has local variations in thickness that introduce 6-7% intensity changes at 8 keV.

X-Ray Masks

Hard x-ray masks for DXRL require a gold absorber thickness of 20-50 µm on a silicon or beryllium substrate. Beryllium offers several advantages over silicon as the carrier material for hard x-ray masks, including greater mechanical stability, greater thermal conductivity, and better match of thermal expansion to PMMA. Thus, we have begun an investigation of the manufacture and use of beryllium x-ray masks.

A soft x-ray (~1.5 keV) lithography-electroforming process can be used to achieve the needed absorber thickness, edge acuity, and mask dimensions (> 3 in x 3 in). To fabricate the masks, a bilayer process using a conformal soft x-ray mask has been adopted. A 2 µm gold absorber layer is fabricated directly atop a 60 µm spin-coated and lapped PMMA layer on a coated 1 mm beryllium substrate using UV photolithography and electroforming. The 2 µm patterned gold is used as the mask to expose the 60 µm PMMA layer using soft x-rays. The top gold layer is then removed, the PMMA developed, and a 20-50 µm gold absorber is electroformed in the patterned PMMA.

The sensitivity of the beryllium to corrosive attack makes it necessary to use protective coatings, such as silicon nitride, in order to enable the beryllium to withstand the fabrication processes used. The stability of these coatings to x-ray exposure is an important consideration, and exposure-induced damage to the masks has been examined. While a CVD silicon nitride coating offers adequate protection through the fabrication steps, substantial adhesion loss of the gold absorber was noticed upon exposure to x-rays. Also, pin-holes in the silicon nitride coating make it inadequate for protection from the strong corrosives used for stripping the expensive beryllium substrates for reuse. Hence, applicability of other coatings, such as boron and diamond, is being examined.

Resist Characterization

For fabrication of microstructures using DXRL, we use a thick (> 1 mm) PMMA resist layer consisting of a linear polymer (M_w ~5,000,000) supplied in sheets. The absorbed dose in the PMMA is only a function of the x-ray spectrum that reaches a particular depth of the resist, the weighted atomic absorption coefficient of the PMMA, the incident power, and the exposure time.

Thus, the dose gradient between the top and bottom of the PMMA is due to the spectrum of the bending magnet source after being modified by mirrors, filters, and mask. For PMMA, the typical dose requirements to achieve correct exposure are: the maximum dose to avoid damage (< 20 kJ/cm^3), and the minimum dose to ensure proper development (> 5 kJ/cm^3).

The dose requirement to achieve the correct resist exposure, however, certainly depends on the PMMA/development system performance. This is a function of the PMMA sheet composition, developer chemistry, and development parameters. But for high energy exposure of thick sheets, the sheet thickness and the final spectral distribution may also affect performance, so that exposure and development must be characterized and optimized for these conditions. Moreover, it is necessary to determine, with exposure to higher energy x-rays (10-30 keV), if the required absorbed dose remains the same and to what extent reciprocity failure is dependent on x-ray energy and power, as well as PMMA thickness.

We have exposed PMMA sheets of various thicknesses (approx. 1, 2.5, 6 mm) under different beamline configurations (beam current, mirror angle, filtration, mask substrate) to vary the x-ray spectral distribution. The exposed molecular weight distribution was determined by gel permeation chromatography (GPC), and the development rate of the resist was measured as function of dose for two development systems (GG, MIBK), (Figure 4). The effects of dose rate on PMMA due to varying incident power has been examined. With these results, we have been able to determine the necessary exposure and development conditions required to carry out DXRL at beamline 2-BM.

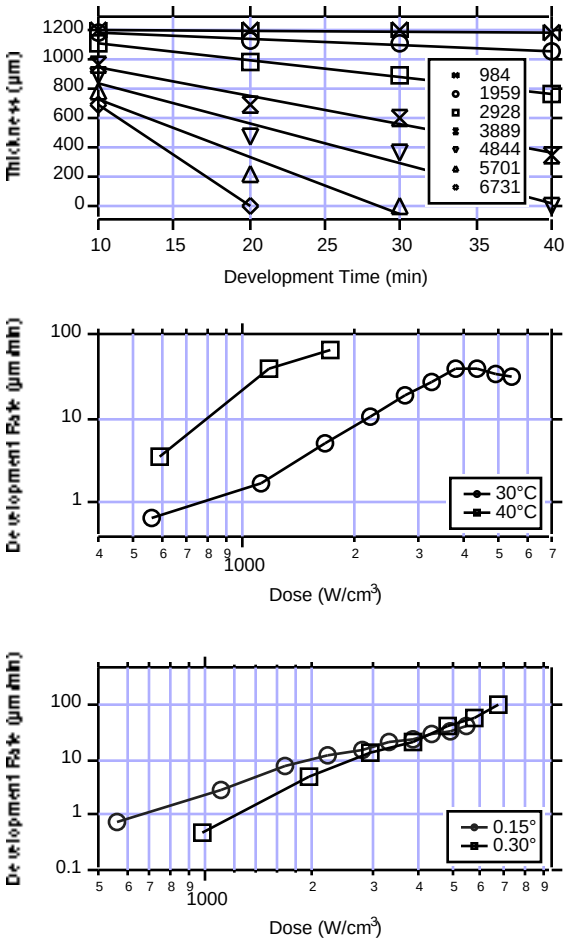

Fig. 4. Development rate of PMMA in MIBK for different exposure and development conditions. Top: PMMA loss for mirror at 0.3° and MIBK at 30° C at different dose levels. Middle: Development rate for mirror at 0.15° in MIBK at temperatures 30°C and 40°C. Bottom: Development rate in MIBK at 30°C for mirror angle at 0.15° and 0.3°.

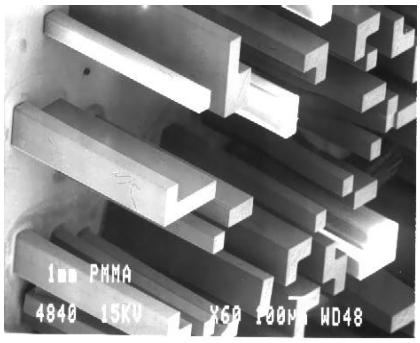

Fig. 5 SEM micrograph of structures of coded aperture patterns in a 1-mm-thick PMMA resist.

First Structures

In addition to resist characterization, we have exposed and developed structures in 1-mm-thick PMMA. Initially we have concentrated on micro-machining x-ray apertures. In collaboration with NASA Goddard Space Flight Center, we have been working on a prototype coded aperture for x-ray imaging. The structure consists of a pseudo-random array of 100 μm x 100 μm pixels. We have reproduced this structure in 1-mm-thick PMMA (Figure 5) on silicon and beryllium substrates. Ultimately, the PMMA structures will be used to electroform the final apertures in gold. This technique will be applied in the near future to the micromachining of x-ray pinholes, slits, and slit arrays that could be used at synchrotron radiation facilities such as the APS.

B. Lai, D.C. Mancini, F. DeCarlo, S.S. Bajikar, APS Experimental Facilities Division

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Publications

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Randall, K. J., J. Z. Xu, D. Graessle, J. J. Fitch, S. DiFonzo, B. R. Mueller, and W. Jark, Reflectivity Measurements of Multilayer Optics for Use on the Advanced Photon Source Soft X-ray Beamlines, *NSLS Annual Report 1996*

Who's New

Linda J. Shoudis joins SRI CAT in the capacity of CAT Administrative Secretary. She has worked in APS Experimental Facilities Division Office over the last four years.

Calendar of Events

May 12-16 ,1997
1997 Particle Accelerator Conference
Hotel Vancouver, Vancouver, B.C., CANADA

June 17-20 ,1997
1997 National Conference on Synchrotron Radiation Instrumentation
Cornell University, Ithaca, NY

July 13-17, 1997
Oxford, UK. Fifth International Conference on Surface X-ray and Neutron Scattering

July 27 - August 1, 1997
Sagamore XII - Charge, Spin and Momentum Densities
Prince Albert National Park, Saskatchewan, CANADA

July 27 - August 1, 1997
SPIE International Symposium on Optical Science, Engineering, and Instrumentation
San Diego Convention Center, San Diego, CA

August 3-8 ,1997
Gordon Research Conference on X-ray Physics
Plymouth State College, Plymouth, NH

August 4-8,1997
6th International Conference on Synchrotron Radiation Instrumentation (SRI 97)
Himeji Citizens Hall, Hyogo, JAPAN

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